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XII. *Experiments on the Flow of Heat in Metal Sheets.* By

SIDNEY SKINNER, *M.A., Principal of the South Western Polytechnic Institute, Chelsea.*

RECEIVED MARCH 7, 1916.

A METHOD of showing to a class the conductivity of heat along a bar is to place the bar under a specially prepared paper which changes colour with heat. The experiment is not satisfactory, because paper is too poor a conductor, and the colour effect has no definite edge. I attempted to find a remedy for the poorness of conductivity by backing the paper with a metal plate. This, although it showed in a general way the flow from a tongue of metal into a sheet, was still not satisfactory on account of the indefiniteness of the colour effects. The metal plate used was cut from a sheet of tinned iron, and I noticed that the edge of the region where the tin had melted could be seen very definitely. The tin melts with a sharp edge which forms an isothermal or equi-temperature line corresponding to its melting point—227°C. Inside this sharp line other equi-temperature regions are shown by the oxidation colours of tin. Each oxidation colour seems to correspond to a definite temperature. When the melted tin solidified the crystals arranged themselves differently to the arrangement in the original plate, and the equi-temperature line may be very sharply developed

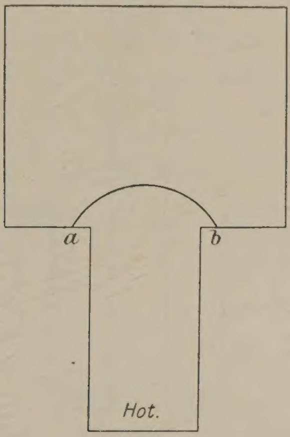


FIG. 1.
ab is the curve of melted tin.

by washing the surface with a mixture of bleaching powder and hydrochloric acid. I have used this plan of observing the line of melting on the surface of tinned iron to examine the flow of heat in iron sheets cut in different shapes with a view of comparing the equi-temperature lines with what would be the equi-potential lines in current flow through similarly shaped sheets. This method of demonstrating the equi-temperature lines is similar to that used by de Sénarmont, "Ann. Chim. Phys.," 21, 457, 1847, who used a wax coating, and to that used by other experimenters, including Voigt, "Wied. Ann.," 60, 350, 1897, who used elaidic acid mixed with wax and turpentine.

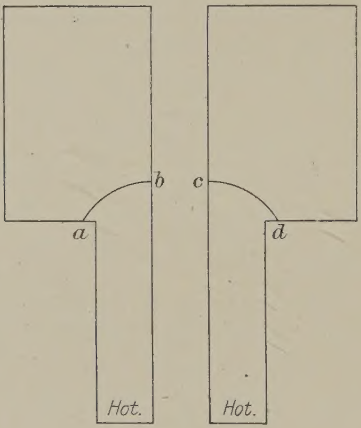


FIG. 2.
ab, *cd* are the curves of melted tin.

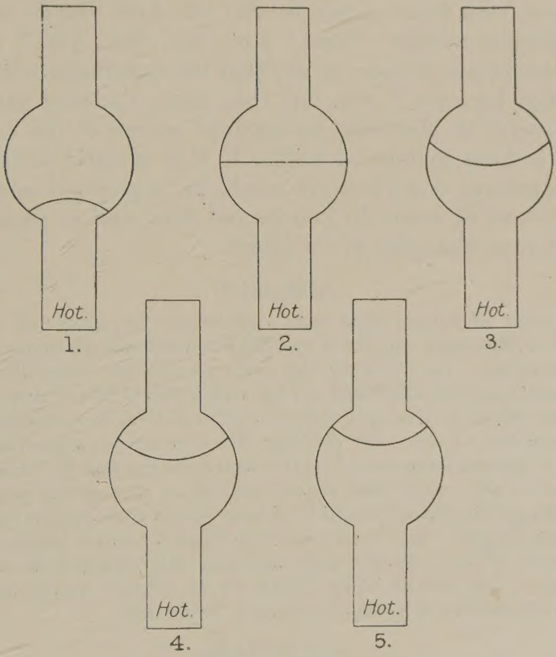
One problem examined was the flow of heat from a tongue into a large sheet. The sheet was placed on a tile or piece of asbestos, and the tongue was heated by a bunsen flame. As the heat proceeded into the sheet the melting of the tin could be watched, and it was noticed that the edge of the melted tin took the shape of an ellipse, with the minor axis in the direction of the tongue. This is illustrated in Fig. 1.

We may compare this with the flow of electricity from a tongue into a plate. Equi-potential lines take the same form as the equi-temperature lines.

It is an electrical law that if a plate be cut along a line of flow no change will take place in the equi-potential lines in the portions which are formed by the cut. I have made a similar experiment with the flow of heat in a tinned sheet by cutting along the tongue and through the sheet in the direction of flow. In the two portions I have studied the flow of heat separately. On putting them together the equi-temperature line was the same as in the uncut sheet. This is illustrated in Fig. 2.

With these results should be compared the equi-potentials as calculated and mapped experimentally by Prof. C. H. Lees, "Proc." Physical Society of London, XXI., 309, 1909.

Another problem I have examined is the flow of heat into a circular disc and out from a circular disc. A piece of tinned iron is taken, and the circular disc cut from it with two tongues to it, one for the source of heat, and the other for the sink. When this is heated an equi-temperature line exactly analogous to the equi-potential line in current flow may be observed. By taking a number of similar sheets, equi-temperature lines corresponding to different extents of flow may be obtained. Where the heat enters the equi-temperature line is concave to the entrance, and where the heat leaves the line is convex to the entrance. These results are illustrated by diagrams, Fig. 3, and



1. 2. 3. 4. 5.

FIG. 3.—VARIOUS STAGES OF FLOW.

if a number of these diagrams are prepared and placed in a thaumatrope the flow of the heat in and out may be demonstrated.

Various shaped plates have been cut out and examined. Among these I may mention an L-shaped plate to show the flow round the right angles ; a plate with a narrow neck in it ; a plate cut in the form of a section of an air-cooled engine to show the influence of the ribs on the outer wall of the engine.

The similarity between the equi-temperature and the equi-potential in current flow is well shown by comparing the figures obtained with those given by the late Prof. Grylls Adams in his Bakerian lecture, " Proc." Roy. Soc., Vol. XXIV., 1875.

In conclusion, I desire to say that the experiments have been described because it was felt that other teachers would find them useful to illustrate the general nature of the equi-temperature lines in flow of heat. If it is desired to make the results precise, some method would be required to control the flow of heat between the source and sink, and to prevent loss of heat from the sides of the plates.

ABSTRACT.

If a sheet of tinned iron be heated locally by means of a Bunsen burner or blowpipe the tin is melted for a certain distance from the heated region. On allowing the sheet to cool the resolidified tin is separated from the unmelted tin by a very sharp line of demarcation. This line gives us the equi-temperature curve corresponding to the melting-point of tin. By pushing the heating to a greater or less extent a series of such equi-temperature curves can be obtained for a sheet of any particular shape heated at any given point. The cases shown illustrated the flow of heat into a rectangular plate from a heated tongue ; into a circular disc from a heated tongue ; round the corner of an L-shaped strip and into the vanes of an air-cooled cylinder. The results were shown to be closely analogous to the flow of electricity in similarly shaped conductors.

DISCUSSION.

Dr. R. S. Willows said a similar method had already been used by Voigt and his students to compare the thermal conductivities of different metals. They employed an organic substance which melted about 41°C. and gave a very sharp line on resolidification. Their method of heating was to place the metal strip on a red-hot copper block.

The President asked if the change of colour of mercuric iodide could not be used for this purpose.

Mr. Ezer Griffiths mentioned that if a sheet of steel be heated at the centre by means of a blow-pipe, then, on cooling, a bright circular wave may be seen travelling towards the centre due to recalescence. The converse effect was said to be observed during heating. The heat-indicating paints were the double iodides of copper-mercury (scarlet) and silver-mercury (yellow). Both darkened on heating, the former at 87°C. and the latter at 45°C., the change being reversible. They could be prepared by adding a solution of $CuSO_4$ or $AgNO_3$ to a solution of KI, redissolving the precipitate and adding a solution of $HgCl_2$. Experiments involving the use of these paints are described in "Light, Visible and Invisible," by Prof. S. P. Thompson.

The AUTHOR said he was glad to hear about Voigt's experiments. He had seen the recalescence experiment mentioned by Mr. Griffiths. One trouble with paints used as heat indicators was that there was usually a considerable lag between the temperatures at which the change took place on heating and on cooling. Moreover, the line of demarcation was not very sharp.

XIII. *The Absorption of Gas by Quartz Vacuum Tubes. By* R. S. Willows, *M.A., D.Sc., and* H. Trevelyan George, *M.A.*

Received March 14, 1916.

It is a common experience to those who work with vacuum tubes that, once the electrodes are freed from gas, the continued passage of a discharge lowers the pressure, and the tube eventually evacuates itself to such an extent that further discharge becomes impossible. This gives rise to much trouble in X-ray technique and, as gas-pressure regulators have to be added, complicates the construction of the tubes. These disadvantages have only recently been surmounted in the well known, but costly, Coolidge tube. It is, therefore, a matter of great practical importance to gain some knowledge of this process of self-evacuation.

The first systematic investigation appears to be that of Willows,* who came to the conclusion that the absorption was the result of chemical actions between the gas and the walls of the tube. The fact that nitrogen was absorbed as well as other gases was at that time a theoretical difficulty, which the subsequent researches of Prof. Strutt on active nitrogen have finally removed. Vegard† has drawn from Willows' results the conclusion that the gas is driven into the cathode ; but he apparently failed to note that absorption is also produced by the *electrodeless* ring discharge. Campbell Swinton‡ thinks that the occlusion is entirely a mechanical effect, the gas being fired into the glass, like a bullet into a target, and retained there. He supports his theory by some striking and beautiful experiments. S. E. Hill§, at Willows' suggestion, used the electrodeless discharge in a number of bulbs made of different kinds of glass, and comes to the conclusion that chemical effects are capable of explaining the results.

One feature of Hill's experiments, which has a bearing on the observations which follow, is the fact that a bulb can be fed with a gas, *e.g.*, hydrogen, until its appetite is very greatly diminished, but can be restored to its original activity by allowing it to absorb another gas, *e.g.*, air. This, together with the fact that different glasses absorb in very different degrees, in our opinion points clearly to chemical action as, at least, one of the main causes of the absorption.

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* "Phil. Mag.," April, 1901.

† "Phil. Mag.," 18, 477, 1909.

‡ "Proc." Roy. Soc., 81, 453, 1908. Other references to Mr. Swinton's work will be found here.

§ "Proc.," Phys. Soc., Dec., 1912.

The present communication is a continuation of Hill's work. Owing to the chemical inertia of quartz it was considered that experiments on a tube of this material would be of interest. A spherical bulb 7-8 cm. in diameter was used; it was connected through a mercury seal to a pump and a McLeod gauge reading to 1/500 mm. An electrodeless discharge was produced in the usual manner by means of a 6 in. coil. The zinc discharge knobs were carefully polished at frequent intervals in order to keep the current through the gas as steady as possible; with the same object the coil was driven by a mercury-jet interrupter and the spark was blown out by an air blast.

The method of making observations was as follows: After proper preparation the tube was mounted on the apparatus, washed out several times with the gas to be used, and pumped down to a pressure at which the discharge would pass. For air this was about $\frac{1}{3}$ mm., but for hydrogen about 1 mm. The coil was run for a certain interval and the change in pressure that the discharge had produced was noted on the gauge; if necessary the pressure was then slightly reduced before further observations were made. In this way the whole range of pressure was covered in which an electrodeless discharge was possible. In the tables below the pressures are given in gauge readings. Initially the first bulb was cleaned out with chromic acid and distilled water before it was used. In the early experiments, in which air was used, it was thought that the problem of stopping the absorption was finally solved; for a discharge was passed under various pressures for a total period of several hours without causing the slightest absorption; there was, if any change at all, a very slight increase in the pressure. When, however, the bulb was washed out with hydrogen the discharge immediately caused an absorption of gas, as is seen from the Table below.

TABLE I.—*Showing the First Absorption of Hydrogen.*

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
10	163	4
20	122	2
15	94	nil

A fresh charge of hydrogen was allowed to stand in the apparatus for a few hours and further observations were made. This was repeated with fresh supplies of gas in succeeding days, during which it was noticed that the activity of the quartz was gradually increasing, until it finally reached a maximum and then gradually decreased. This is shown in Table II.

TABLE II.—*Showing the Absorption of Hydrogen a few days later than in Table I.*

Period of discharge.	Mean pressure.	Decrease of pressure.
10	242	5
10	182	5
10	136	5
5	100	12
10	70	42
10	32	25
4*	14	3
* The discharge failed to pass after this interval.		
	A few days later.	
10	107	2
10	72	9
10	49	6
10	31	4

During the last set of readings it was noted that the discharge was exceptionally good; the failure to absorb so readily as before cannot, therefore, be ascribed to faulty conditions of the experiment.

These Tables agree with Hill's experiments in showing that the appetite of a tube for hydrogen can be greatly diminished after a certain stage. This agreement extends still further, for the bulb was now filled with air and a discharge passed, when it was found that if the pressure was less than 90 the absorption was as large as, and sometimes larger than, with hydrogen. At pressures greater than 90 the current usually caused a very slight evolution of gas. Although the experiments were run for several days very little fatigue effect was noticed with air. Further fillings with hydrogen showed that this gas was now very actively absorbed.

A review of all the experiments shows that, no matter what the treatment to which the bulb has been subjected, the discharge never causes the pressure to rise when hydrogen is used, except for a few doubtful increases which occur when the gas has been standing at a considerable pressure in the bulb for some time. These exceptions may easily be due to gas condensed on the walls. With air slight evolutions nearly invariably take place at pressures greater than 100, while at lower pressures gas is gradually absorbed.

It will be seen from this description that our results with quartz are very similar to those of Hill with glass. The chief difference is that, in our experiments, a bulb has become actively absorbent for air although it was altogether inactive initially.

A possible explanation of this last result might be the presence of a layer of hydrogen condensed, or more properly speaking, adsorbed on the walls of the bulb, either on account of electrical attractions or from some other cause. It is well known that such layers of gas do exist when a bulb is first exhausted. The air might then combine with this and so apparently be absorbed, as any water vapour would be taken up in the drying bulbs. Such a layer of air or hydrogen might also account for the evolution at the higher pressures, for the heat of the discharge may possibly drive off gas to such an extent as to mask the absorption.

The following experiment shows that this is not the correct explanation of the absorption of air. The quartz bulb was made red hot and the evolved gas was pumped off until further heating caused no change in the pressure. On admitting a small quantity of air and discharging the coil the absorption was found to be larger than ever. It may also be mentioned that similar heat treatment was applied to the bulb when it was first received, without, as has been shown, causing the slightest adsorption of air. The hydrogen, if present, must therefore be in the combined condition; and further, when the bulb was blown the treatment was such as to leave it free from combined hydrogen. It must also be remembered that, according to Freundlich*, both oxygen and nitrogen are much more strongly adsorbed than hydrogen. Table III. shows the absorption of air after the bulb had been strongly heated, pumped out, and a small quantity of air re-admitted.

TABLE III.

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
$4\frac{1}{2}$	43	51
$4\frac{1}{2}$	38	41
$1\frac{1}{4}$	38	20

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* "Kapillarchemie," p. 96, *et seq.*

When the bulb had been treated in this manner it was found that further heating caused an evolution ; but a similar effect was found even without the discharge, and is no doubt due to gas adsorbed on the walls. It is uncertain whether all the absorbed gas can be recovered by heating ; this, together with further details, we hope to investigate later.

Our experiments with this bulb remind us strongly of the formation of the active plates in a Planté accumulator, if the absorption of air be taken to correspond to the discharge of the cell and that of hydrogen to the charging. Just as, initially, the cell must be charged before it can supply a current, so must hydrogen be absorbed before an absorption of air takes place ; and as these processes are alternated the surfaces of both cell and bulb become more active.

A second bulb was now tried, hydrogen being the first gas used. Observations were made from pressures of 200 downwards, but to save space only a few of these are given in Table IV.

TABLE IV.

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
5	117	7
5	110	3
5	80	1
5	61	1
5	48	0
5	36	0
5	21	0

The Table shows that the absorption was small and had a definite limit but, as before, it gradually increased with successive doses of hydrogen. When a few charges had been absorbed air was admitted and was found to disappear from the first. The second bulb, in fact, behaved exactly like the first did after hydrogen had been absorbed.

In spite of the chemical inertness of quartz we regarded chemical actions between the gases of the discharge and the bulb as, at least, a possibility. If they involved the quartz directly our experiments might be explained as follows : Initially the walls consist of SiO_2, and if this cannot be further oxidised no air absorption should occur. This is what takes place. When hydrogen is admitted and the discharge is passed it may first reduce some of the silica and may then form silicon hydride. If the hydrogen is now replaced by air both oxygen and nitrogen are absorbed ; hence we must suppose that not only is the oxide reformed, but compounds containing nitrogen (nitrides ?) also appear. We tried to bring about similar effects by chemical treatment. The bulb was washed out with stannous chloride with the idea of reducing any oxidation product that had been formed, and thereby diminishing the absorption of hydrogen. Tests showed that this did not produce any clearly marked effects at first, but as they progressed it appeared that the appetite of the tube for hydrogen was now more easily satisfied.

A similar, but more marked effect, was found if the stannous chloride was replaced by SO_2 solution ; after three charges the bulb refused to absorb hydrogen from a pressure of 100 downwards—the region where previously the absorption was most strongly marked.

Hot aqua-regia was also used with the idea of reducing the absorption of air, but we did not succeed in doing this. The aqua-regia brought about more quickly the state in which hydrogen is not absorbed. It is, therefore, doubtful whether these effects are genuine chemical effects ; they may rather have produced adsorbed layers of gas on the bulb, whose gradual release masks the absorption. This point and others connected with adsorbed gas were under consideration when the work had to be suspended, but we hope to return to them later. The matter should prove easy to settle in the case of a substance which can be so strongly heated as quartz.

With regard to the relation of our experiments to those of Mr. Swinton we propose to say very little. Even when the electrodes in his experiments are outside the tube there is considerable bombardment of the glass and intense local heating, and it is doubtful whether we are testing the same effects as he does.

It was thought at one time that there were visible chemical changes on the surface of the bulb, as sometimes there appeared a black deposit at the neck of the bulb and, less frequently, in the plane of the discharge. This has also been noticed by Hill. It was found to be readily soluble in cold aqua-regia and was volatilised below a dull red heat ; most probably it is some compound of mercury. It is unlikely to be silicon as the melting point of this element is 1,400°C. We tried to keep mercury vapour out of the bulb by packing the leading tube with gold leaf, but this did not prove a satisfactory filter, as examination with a Hilger wave-length spectroscope readily showed. We understand that the absorptive power of the leaf depends on its physical condition ; only annealed leaf is a satisfactory absorbent. Various annealings, however, still left us unsuccessful.

While examining the spectrum we were interested to note the way in which the hydrogen spectra varied in intensity. At about 1 mm. pressure the primary spectrum of hydrogen was all that could be seen ; this at first increased in intensity as the pressure was lowered, then gradually disappeared. At the same time the mercury spectrum became more prominent and also a very fine secondary spectrum of hydrogen appeared. This could only be seen at a distance of a few millimetres from the walls, *i.e.*, in the strongest part of the ring discharge.

ABSTRACT.

The experiments are a continuation of those of Willows (" Phil. Mag." April, 1901) and Hill (" Phys. Soc.," December, 1912) on the absorption of gas which is brought about by electrical discharges. A new quartz bulb does not absorb air, but if it be fed with repeated doses of hydrogen—which are absorbed when an electrodeless discharge is passed—it then becomes very active. If discharges in hydrogen are alternated with those in air the bulb can be made to absorb large quantities of either gas, and the activity with each gradually increases. The authors reject the theory of surface absorption and, in their own experiments at least, also Swinton's theory that the gas is shot into the walls and held there. It is supposed that chemical actions occur with air, and oxidation products are formed ; these are reduced by hydrogen. The process is compared with the formation of the plates in a Planté cell ; the absorption of hydrogen corresponding to the charging, and that of air to the discharging of the cell. Attempts to produce the same effects by chemical treatment are partially successful, particularly in fatiguing the bulb so that no further absorption takes place. The conditions under which the primary and secondary hydrogen spectra appear are also described.

DISCUSSION.

Mr. A. Campbell Swinton said he was very much interested in the subject. It was true that most of his experiments were done with tubes having electrodes and there was very considerable heating. Under the bombardment of the cathode particles the inner surface of the glass may attain a very high temperature for a very short space of time. Sir J. J. Thomson had thought that it might almost become fluid and absorb the gas by ordinary diffusion. Sir J. Larmor, on the other hand, had conceived the molecules of gas to be hammered into the glass like tin tacks by the cathode particles. Some of his experiments had been done with external electrodes of tinfoil tied round the outside of the tube. He had also obtained absorption of helium which was not known to combine chemically with anything.

Dr. Bryan described some experiments he had been making with a vacuum valve at pressures less than 1/1000th mm. Normally the electrodeless discharge will not work at this pressure, but it does so when a current is passed through the glower (tungsten filament). Under these circumstances the pressure rises, although, after the valve has been running for some time, the current in the filament when running by itself produces a decrease in pressure.

Dr. ECCLES, referring to the failure of gold leaf in certain circumstances to absorb mercury vapour, said that some workers were using silver for this purpose. It seems to have been used successfully for reducing mercury vapour pressure down to, but not beyond, a certain limiting vapour pressure.

Dr. H. S. ALLEN said that if a tube were coated with silver by spluttering from silver electrodes, the layer so obtained was said to absorb mercury vapour very readily.

Dr. WILLOWS, in reply, said that Mr. Campbell Swinton's results with helium were not conclusive, as it was not certain that they were dealing with the same phenomenon. The discharge in a tube with external electrodes was not an electrodeless discharge at all. There was still cathode ray bombardment and strong local heating. It would be interesting to see if the experiments with helium could be repeated with a true electrodeless discharge free from any electrostatic effects. He thought Dr. Bryan's results could all be accounted for by gas coming out of the metal itself. He had not used silver to absorb mercury vapour because of the difficulty of getting it free from air. Mr. Harlow about two years since showed the Society an experiment similar to the one described by Dr. Bryan.

XIV. *A New Method of Determining Ionic Velocities.*

By Constance Harrison Griffiths, *B.Sc., Research Student, Birkbeck College.*

Received February 25, 1916.

Introduction.

The object of the research was to test the practicability of a method of determining ionic velocities, which can be carried out with the resources of an ordinary physics department and which requires little or no skill in chemical manipulations.

The electrolyte chosen for the tests was an aqueous solution of copper sulphate.

In the Hittorf and kindred methods the changes in the electrolyte produced by the passage of the current are determined by chemical analysis; in the method to be described the total change in weight of the cathode and the electrolyte in its neighbourhood is obtained by direct weighing, and allowances are made for the change in volume of the cathode and for the changes in volume of the liquid surrounding the cathode, as it changes in density. The cathode was situated in a cylindrical vessel closed at the upper end and open at the lower end.

The cathode and the containing vessel were suspended from the arm of a balance and hung in a tank containing an aqueous solution of copper sulphate.

Theory of the Method.

Let the diagram represent the cathode and the containing vessel.

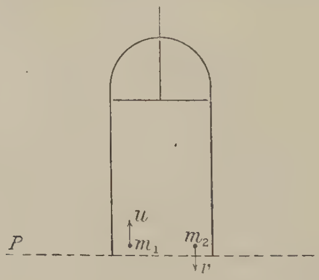


Fig. 1.

Let m_1 be the mass of the cations per cubic centimetre.

,, u cms./sec. be the component of their velocity upwards relatively to the liquid.

Let m_2 be the mass of the anions per cubic centimetre.
,, v cms./sec. be the component of their velocity downwards relatively to the liquid.
,, c=the current in amperes.
,, A=area of cross-section of the lower end of the electrode vessel in square centimetres.

Consider passage of ions across the section P.

Then *loss of weight* in electrode vessel per second would equal

$$(m_2v-m_1u)\,A \text{ grammes}$$

if the liquid were at rest. Allowance must be made for the movement of the liquid.

Let q=the quantity in coulombs of electricity required to deposit 1 gramme of cations; then mass of deposit per second $=c/q$ grammes.

If the density of the deposit is d, *increase of volume of electrode* per second$=c/qd$ cubic centimetre.

Total mass of salt in cathode vessel diminishes at the rate of $(m_1+m_2)Av$ gms./sec., since m_2Av grammes of anion leave the vessel per second, and there are always equal numbers of $+^{ve}$ and $-^{ve}$ ions in the liquid in the cathode vessel. When a salt is dissolved in water there is in general an *increase in volume.*

Let δ=the increase in volume produced by dissolving 1 gramme of salt.

Then decrease in volume of solution in vessel$=(m_1+m_2)Av\delta$ cubic centimetres.

$\therefore$ Total decrease in volume in vessel$=(m_1+m_2)Av\delta-c/qd$ cubic centimetres.

Unchanged liquid to this amount will, therefore, enter the vessel, and if its density is ρ the gain in weight will be

$$\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho \text{ grammes.}$$

$\therefore$ Total loss in weight of the suspended system

$$=(m_2v-m_1u)A-\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho \text{ grammes} \quad . \quad (1)$$

This is one relation. Now there is a second relation.

Let N=number of gramme equivalents of copper per cubic centimetre and e=quantity of electricity associated with 1 gramme equivalent; then

$$Ne(u+v)A=\text{total current in amperes.} \quad . \quad . \quad (2)$$

Summary.—Therefore we have the two equations

1. $(m_2v-m_1u)A-\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho$

$=$total loss of weight of suspended system per second.

2. $$Ne(u+v)A=c.$$

SECOND METHOD OF CONSIDERING THEORY.

Let a=absolute velocity of cations upwards.
b=absolute velocity of anions downwards.
x=velocity of liquid upwards across the lower end of the cathode vessel.
n=concentration in gms./cc. of solution.

And let the remaining symbols have the same meaning as before Then, clearly,

$$a=u+x$$
$$b=v-x.$$

Consider the passage of ions across the section P, *i.e.*, across the lower end of the tube.

The total mass of anions crossing the section downwards equals m_2bA per second, and the total mass of cations crossing the section upwards equals m_1aA per second.

Thus the loss in mass per second of the cathode vessel due to the movement of the ions equals $(m_2b-m_1a)A$.

Since m_2b of anions leave the cathode vessel, and since there must be a corresponding loss of the cations in solution in the cathode vessel, it follows that $(m_1+m_2)bA$ equals the diminution in the quantity of salt in solution in the cathode vessel. There is a gain in the quantity of water in the cathode vessel owing to the velocity x of the liquid upwards.

This gain per second$=xA(\rho-n)$; since $(\rho-n)$ is the mass of water per cubic centimetre of solution.

Thus total loss of weight of cathode vessel per second equals

$$(m_2b-m_1a)A-xA(\rho-n).$$

When a salt is added to a solution there is in general an increase in volume of the solution.

Let δ=the increase in volume produced by dissolving 1 gramme of salt. As is shown above, $(m_1+m_2)bA$ equals the mass of salt extracted per second, as the result of the electrolytic operations, from the cathode vessel.

But the liquid moves upwards x centimetres per second, and introduces $x(m_1+m_2)A$ grammes of salt into the cathode vessel.

Thus, the salt lost by the solution originally in the cathode vessel equals $(m_1+m_2)bA+x(m_1+m_2)A$;

$$i.e.,\ =(m_1+m_2)(b+x)A, \quad \text{or } (m_1+m_2)vA.$$

It is clear that the diminution in volume due to the diminution in the salt in the cathode vessel equals $(m_1+m_2)vA\delta$. Account must now be taken of the change in volume of the cathode. Then, as before, the increase in the volume of the cathode per second equals c/qd.

Thus $$xA=(m_1+m_2)vA\delta-\frac{c}{qd}.$$

Substituting this value of xA in the expression for the rate of loss of total weight of the cathode and cathode vessel we obtain

$$(m_2b-m_1a)A-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n).$$

Substituting $a=u+x$ and $b=v-x$ we obtain

$$(m_2v-m_1u)A-(m_1+m_2)xA-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

i.e., $$(m_2v-m_1u)A-(m_1+m_2)\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}$$
$$-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

i.e., $$(m_2v-m_1u)A-n\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}$$
$$-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

i.e., $$(m_2v-m_1u)A-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho), \quad . \quad . \quad (1)$$

which is the same equation as was obtained by the other method of considering the theory.

By reasoning exactly similar to that used in the first method we obtain

$$Ne(a+b)A=c;$$

whence $$Ne(u+x+v-x)A=c,$$

and $$Ne(u+v)A=c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is exactly the same as the second equation previously obtained.

APPARATUS.

In the diagram B is the plan of a balance from which hangs the cathode K and the cathode vessel C.

A is the anode and anode vessel, and T the tank which contains the solution used for the experiment.

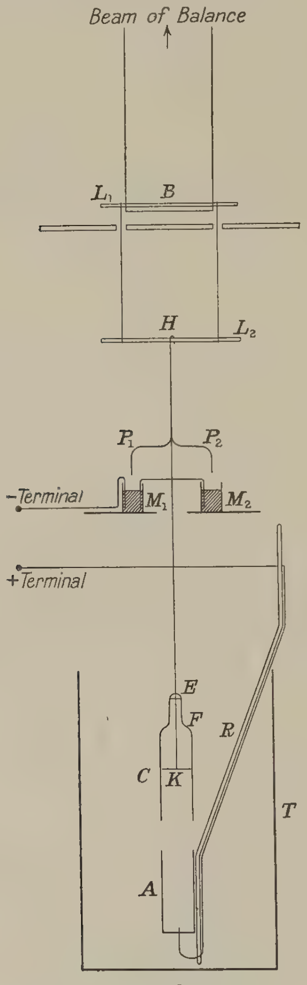


FIG. 2.

DETAILS OF APPARATUS.

Cathode.—The cathode consists of a disc of copper 2·7 cm. diameter, perforated by two holes. It fits loosely into the cathode vessel C. The *cathode vessel* consists of a glass tube 8·9 cm. long and 2·7 cm. diameter, open at the lower end. At the upper end the cathode vessel is narrowed and terminates in a piece of 2 mm. bore tubing about 3 cm. long. The cathode is situated about halfway up the cathode vessel, so that the weaker solution produced by the passage of the current may pass through the holes in the cathode and to the top of the cathode vessel.

Suspension of Cathode.—The cathode vessel and the cathode are suspended by means of gutta-percha-coated copper wire. This wire is attached to the cathode at its lower end by being scraped clear of insulation at that point and threaded backwards and forwards through four holes bored near the centre of the cathode.

The insulated wire passes vertically up from the cathode and through the 2 mm. bore tubing EF, into which it fits somewhat tightly, and into which it is sealed at the top with a small quantity of Chatterton cement.

Thus the cathode vessel is completely closed at the top. About 34 cm. above the cathode vessel the suspension wire terminates in a hook which passes over a glass rod suspended from a balance pan.

Electrical connection with the cathode is effected by means of two plantinum points attached to the suspension wire near the top.

Anode.—The anode consists of a spiral of thick copper wire with a lacing of thin wire across two diameters to hold the turns of the spiral in place.

From the centre of the spiral and continuous with it, being part of the same wire from which the spiral was made, a wire passes down vertically till clear of the anode vessel, then bends round and passes up through the liquid and out at the top of the tank.

All this wire, after it leaves the anode spiral, is coated with gutta-percha insulation.

The *anode vessel* consists of a piece of glass tubing 8 cm. long and 2·7 cm. diameter. The anode just fits inside it at the lower end.

Support Rod.—The wire to the anode vessel and the anode vessel itself are bound tightly to a bent glass rod, R, which supports them and holds them in the required position. This rod is clamped above the level of the top of the tank by two firm clips which are carried by a vertical bar fixed in a strong stand.

The anode vessel is set vertically under the cathode vessel so that the distance apart of the two vessels is about 3 cm. This is done before the tank is placed in position.

Current Leads to Cathode.—The suspension wire of the cathode is cleared of insulation at a point near the top, and round it at this point are tightly wrapped two pieces of copper wire. These are bent as in the diagram and terminate in two platinum points. These platinum points dip into two cups of mercury connected together by a thick copper wire. Into one of these cups dips a wire connected to the negative terminal of the cell.

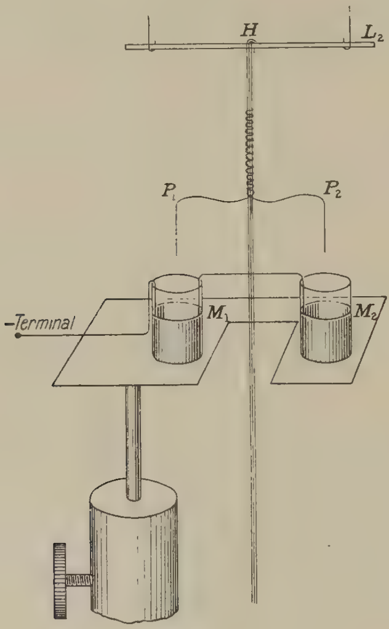


FIG. 3.

The mercury cups are supported by a shelf of wood fixed to a stand of adjustable height. By raising the stand till the platinum points are immersed in the cups the current is allowed to pass. On lowering the stand the points hang free in air, and weighings can be made by means of the balance.

Balance.—The balance used was a Sartorius, and would weigh with accuracy to 0·0001 grammes. It is enclosed in a case in the floor of which two holes were bored beneath and slightly to each side of the left-hand pan. Across the left-hand pan is placed a glass rod painted with shellac. Over this are hooked two short wires of copper, one at each end. These wires pass vertically down, one through each of the two holes in the floor of the case. At the lower end of each is a hook, and these hooks support another glass rod similar to the first. From the centre of this second rod hangs the cathode and cathode vessel by means of the hook at the top of the suspension wire.

Tank.—The tank is a large cylindrical glass jar 29 cm. high, 19 cm. diameter, having a capacity of 8 litres approximately. This tank contains the solution of copper sulphate used for the experiment.

Over the surface of the solution is placed a layer of castor oil (about 100 cubic cm.), for it was found that the weighings taken by means of the balance were very inaccurate when the suspension wire passed straight into the copper sulphate solution from the air, but that when the layer of castor oil was placed over the surface the weighings were very consistent.

The temperature of the solution in the tank is taken by means of a thermometer suspended in the solution, so that its bulb is close to the cathode vessel.

General Arrangement of Apparatus.—The foregoing apparatus—tank, balance, cathode, anode, &c.—are arranged in a thermostat room kept at a constant temperature by means of a thermostat-regulated gas stove.

The wires from the cathode and anode are connected to two terminals, and from these wires proceed to a table outside the thermostat room.

On this table is arranged the rest of the circuit, consisting of a 4-volt secondary cell, a key, an adjustable resistance and a Paul millivoltmeter in parallel with 1 ohm.

Method of Procedure.—The copper sulphate solution was prepared, placed in an aspirator and the air exhausted from it by connecting the top of the aspirator to an exhausting pump for one hour. This was done to prevent any formation of bubbles in the tank. The solution was then kept under a vacuum until it was placed in the tank.

The tank was placed in position under the balance, the cathode being already suspended in position. The anode was moved from its position under the cathode by rotating the vertical bar to which the support rod was attached.

A bent capillary glass tube was now fixed so as to project through a hole in the cathode and to reach to the top of the cathode vessel on the inside. The other end of this tube reached above the level of the top of the tank, and was attached to a rubber tube. Through this capillary tube the air in the cathode vessel was withdrawn.

The solution was then run slowly into the tank through a glass tube reaching to the bottom of the tank. When the surface of the liquid reached the cathode vessel air was withdrawn through the capillary tube, so as to keep the levels of the solution inside and outside the cathode vessel approximately the same.

When the tank was full to within 2 cm. of the top, and all the air withdrawn from the cathode vessel, the capillary tube was removed. The anode was brought back to its correct position and the castor oil was poured on the surface of the liquid.

A thermometer was suspened in the solution and the apparatus was usually left till the next day. On the next day a *weighing of the suspended cathode vessel and cathode* was made and the time noted.

After an interval of about one hour *another weighing was taken* at a noted time. The temperature was also read. The *mercury cups* were then raised so as to make contact with the platinum points, and the current was put on at a definite time and rapidly adjusted to the desired value.

Readings of the current and the time were then taken at intervals. The temperature was also read at intervals.

After a time, which varied from about two hours in the case of the more concentrated solutions to four hours in the case of the less concentrated solutions, the current was stopped at a certain definite time. The mercury cups were lowered and the weight was rapidly taken. After about one hour another weighing was taken to get the rate of change of the weight after the experiment.

The mean of this rate of change and the rate of change before the experiment was taken to be the average rate of change of weight during the course of the experiment, and was applied as a correction to the observed change of weight.

The average current during the time of the experiment was found by taking the average current over the intervals between each two consecutive readings, multiplying each of these averages by the number of minutes in that interval, and finally obtaining the average current per minute from all the results so obtained.

To the results so obtained a correction was made for the zero of the ammeter.

Weighing of the undisturbed cathode vessel and contents made the day after an experiment showed that the change of weight due to diffusion into the cathode vessel might safely be neglected, and proved also that there was no appreciable change in the concentration of the solution towards the lower end of the cathode vessel in the course of an experiment.

SPECIMEN EXPERIMENT.

Experiment No. 12.—

Density of solution (found by means of a specific gravity bottle) = 1·0273.

Time.	Weight.	Current reading in milliamperes.	Temp.
2–5	33·4360	......	20·00
2–48	33·4360	......	20·00
	Mercury cups raised.		...
2–52	...	Current started.	...
2–52–10	...	30·1	...
2–53	...	30·2	...
2–55	...	30·4	...
2–56	...	30·5	...
2–58	...	30·6	...
3– 0	...	30·6	...
3–10	...	30·7	...
3–20	...	30·8	...
3–35	...	30·8	...
3–40	...	30·8	...
4– 0	...	30·8	...
4– 6	...	30·8	...
5– 0	...	30·8	...
5–11	...	30·8	...
5–37	...	30·8	...
5–44	...	30·8	...
5–45	...	Current stopped.	...
	Mercury cups lowered.		...
5–49	33·3499	......	19·95
7–33	33·3504	......	19·90

Time of passage of current = 173 minutes.
Average value of current (corrected for zero of ammeter) = 0·03285 amperes.

Change of weight—

Rate of change of weight before experiment = zero

" " " after " $=\frac{0 \cdot 0005}{104}$ gm./mt. increase.

$$\therefore \quad \text{Corrections} = -\frac{0 \cdot 0005}{104 \times 2} \times 181 \text{ grammes.}$$

∴ Corrected change of weight during experiment

$$= 33 \cdot 4360 - 33 \cdot 3499 + 0 \cdot 000435 = 0 \cdot 0865 \text{ grammes.}$$

$\rho = 1 \cdot 0273$. ∴ $n = 0 \cdot 028205$ (by interpolation from tables in Landolt and Börnstein).

$$\therefore \quad m_1 = \frac{0 \cdot 028205 \times 63 \cdot 6}{159 \cdot 66} = 0 \cdot 01124 \text{ gm./cc.}$$

and $m_2 = 0 \cdot 01697$ gms./cc.

To find δ—

$$\delta = \frac{\text{increment in volume}}{\text{increment in salt}}.$$

If ρ = density and n concentration per cubic centimetre in grammes, let

Mass of water = 1 gramme.

Then Mass of salt $= \frac{n}{\rho - n}$ grammes.

Total mass $= 1 + \frac{n}{\rho - n} = \frac{\rho}{\rho - n}$.

Total volume $= \text{mass} \times \frac{1}{\rho} = \frac{1}{\rho - n}$;

$$\therefore \quad \delta = \frac{\frac{1}{\rho_2 - n_2} - \frac{1}{\rho_1 - n_1}}{\frac{n_2}{\rho_2 - n_2} - \frac{n_1}{\rho_1 - n_1}} = \frac{(\rho_1 - n_1) - (\rho_2 - n_2)}{n_2(\rho_1 - n_1) - n_1(\rho_2 - n_2)}.$$

In this case (from tables), when

$$\rho_1 = 1 \cdot 0254, \; n_1 = 0 \cdot 026209,$$
$$\rho_2 = 1 \cdot 0384, \; n_2 = 0 \cdot 039812,$$

substitute these values in above formula; then

$$\delta = 0 \cdot 04431.$$

Collecting data:

$m_1 = 0 \cdot 01124$ gm./cc.	$m_2 = 0 \cdot 01697$ gm./cc.
$\delta = 0 \cdot 04431$	$\rho = 1 \cdot 0273$
$q = 3045$	$d = 8 \cdot 952$
$c = 0 \cdot 03285$ ampere.	

$$\text{Loss of wt./sec.}=\frac{0\cdot0865}{173\times60}=8\cdot333\times10^{-6}$$

$$N=\frac{0\cdot028205}{79\cdot83}$$

$$e=96{,}550.$$

$\therefore$ in equation (1), $m_2V-m_1U-n\delta\rho V+\frac{c\rho}{qd}=$loss of weight/sec. (where $V=vA$ and $U=uA$).

1st term	$m_2V=$	$0\cdot01697V$
2nd ,,	$m_1U=$	$-0\cdot01124U$
3rd ,,	$-n\delta\rho V=$	$-0\cdot001283V$
4th ,,	$\frac{c\rho}{qd}=$	$1\cdot238\times10^{-6}.$
5th ,, Loss wt./sec.$=$		$8\cdot333\times10^{-6}$

$$\therefore \qquad 0\cdot01568V-0\cdot01124U=7\cdot095\times10^{-6} \qquad . \quad . \quad (\text{A})$$

and in equation (2) $Ne(V+U)=c$.

$$U+V=\frac{c}{Ne}=9\cdot632\times10^{-4}.$$

$$\therefore \qquad V=9\cdot632\times10^{-4}-U \qquad . \quad . \quad . \quad . \quad . \quad . \quad (\text{B})$$

Substitute in equation (A) for V.

$$\therefore\ 0\cdot01568\times9\cdot632\times10^{-4}-0\cdot01568U-0\cdot01124U=7\cdot095\times10^{-6}.$$

$$\therefore \qquad 0\cdot02692U=0\cdot8005\times10^{-5}.$$

$$\therefore \qquad U=2\cdot974\times10^{-4}$$

$$V=6\cdot658\times10^{-4}.$$

A, the area of the end of the cathode vessel$=5\cdot9768$ sq. cm.;

$$\therefore \qquad u=4\cdot975\times10^{-5}$$

$$v=1\cdot114\times10^{-4}$$

and $\frac{v}{u+v}=0\cdot6910.$ Temperature$=19\cdot90$°C.

The value of q, the quantity of electricity in coulombs required to deposit 1 gramme of cation, was found by means of a separate experiment, using the same apparatus and a similar cathode *not* enclosed by a cathode vessel; d was obtained from tables.

The area of the end of the cathode vessel A was found by placing a glass scale in millimetres across the end of the tube, so that the scale was in contact with the tube and reading the diameter of the tube by means of a microscope provided with a scale in the eye-piece. Eight readings were made along four diameters at intervals of 45 deg., and from these the value of A was calculated.

The zero of the ammeter was found by comparing the ammeter readings of a current with—

(*a*) An ordinary copper voltameter.

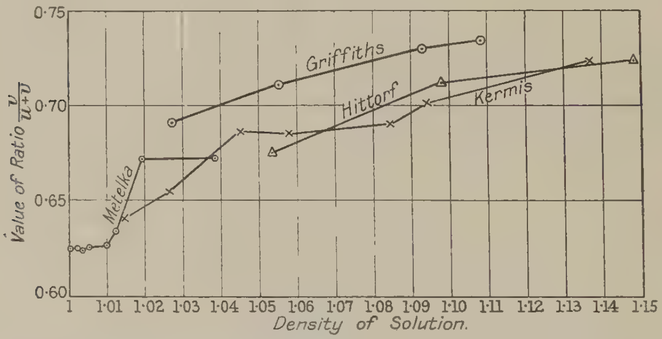
(*b*) A Cambridge thermo-electric potentiometer used across a standard ohm in the circuit and comparison being made against a standard Weston cell.

RESULTS.

A number of experiments were made with solutions of different concentrations, and the results are given in the table on p. 145.

CONCLUDING REMARKS.

It is extremely probable that the method can be employed in the case of other salts from which the metal can be electrolytically deposited on the cathode.



References to Tables of Results, from which curves have been drawn :—

Metelka—" Zeitschrift für Physikalische Chemie." Band XXXVII., 1901. Page 709. (Temp. 18°C—19°C).

Kermis—" Annalen der Physik und Chemie." Band IV., 1878. Page 503 (Temp. 9°C—24°C).

Hittorf—Landolt and Börnstein's tables. Edition III. (Temp. 6°C).

Griffiths—Average values deduced from table. (Temp. 19·6°C—20·3°C).

FIG. 4.

In the case of a salt like potassium sulphate, for example, it is possible that the ionic mobilities could be determined by surrounding the copper anode of the cathode vessel with a solution of copper sulphate of somewhat smaller density than that of the solution of potassium sulphate, thus applying the

Table of Results.

Experiment.	Density	Concentration.	Current in amperes.	Time in seconds.	Change of weight in Gms./sec.	m_1	m_2	δ	u	v	$\frac{v}{u+v}$	Temp. Deg. C.
*1	1·0928	0·09827	0·08180	6,720	$2·061 \times 10^{-5}$	0·03913	0·05914	0·08241	$3·232 \times 10^{-5}$	$8·285 \times 10^{-5}$	0·7190	20·10
*2	1·0928	0·09827	0·04094	7,200	$1·097 \times 10^{-5}$	0·03913	0·05914	0·08241	$1·497 \times 10^{-5}$	$4·266 \times 10^{-5}$	0·7401	20·00
3	1·0928	0·09827	0·07198	9,052	$1·867 \times 10^{-5}$	0·03913	0·05914	0·08241	$2·751 \times 10^{-5}$	$7·382 \times 10^{-5}$	0·7288	20·75
4	1·1083	0·11524	0·06387	8,340	$1·673 \times 10^{-5}$	0·04587	0·06937	0·08241	$2·054 \times 10^{-5}$	$5·615 \times 10^{-5}$	0·7319	20·30
5	1·1083	0·11524	0·06691	8,640	$1·772 \times 10^{-5}$	0·04587	0·06937	0·08241	$2·120 \times 10^{-5}$	$5·914 \times 10^{-5}$	0·7360	19·90
6	1·1083	0·11524	0·03280	15,600	$8·553 \times 10^{-6}$	0·04587	0·06937	0·08241	$1·074 \times 10^{-5}$	$2·908 \times 10^{-5}$	0·7303	19·80
7	1·1083	0·11524	0·03229	13,500	$8·583 \times 10^{-6}$	0·04587	0·06937	0·08241	$1·017 \times 10^{-5}$	$2·861 \times 10^{-5}$	0·7377	19·70
8	1·0554	0·05789	0·03357	13,200	$8·484 \times 10^{-6}$	0·02305	0·03484	0·07092	$2·322 \times 10^{-5}$	$5·699 \times 10^{-5}$	0·7104	19·70
9	1·0554	0·05789	0·03349	15,000	$8·4667 \times 10^{-6}$	0·02305	0·03484	0·07092	$2·320 \times 10^{-5}$	$5·683 \times 10^{-5}$	0·7114	19·80
10	1·0273	0·02821	0·03312	12,900	$8·310 \times 10^{-6}$	0·01124	0·01697	0·04431	$4·951 \times 10^{-5}$	$11·26 \times 10^{-5}$	0·6942	19·30
11	1·0273	0·02821	0·03247	14,400	$8·0972 \times 10^{-6}$	0·01124	0·01697	0·04431	$5·000 \times 10^{-5}$	$10·92 \times 10^{-5}$	0·6861	19·60
12	1·0273	0·02821	0·03285	10,380	$8·333 \times 10^{-6}$	0·01124	0·01697	0·04431	$4·975 \times 10^{-5}$	$11·14 \times 10^{-5}$	0·6910	19·90

* It may be noted that experiments (1) and (2) were of the nature of preliminary experiments, and that after experiment (3) a considerable number of improvements were made in details of the apparatus and in the method of conducting the experiments. These improvements were used in the subsequent experiments (4)–(12).

principle of the Daniell cell. There would be difficulties in determining δ, but the difficulties might not be insuperable.

Another method of determining the mobilities in the case of potassium sulphate would be to have a suspended anode vessel analogous in construction to the cathode vessel described in the Paper, and to have as an anode a metal which would go into solution when the current passes.

The results obtained by the author may be compared with those obtained by Hittorf, Metelka and Kermis by means of the curves drawn on the squared paper (diagram 4).

The comparison would appear to justify the method, but the divergence of the results obtained by previous workers would seem to show that if the progress of physics should demand an accurate knowledge of the values of migration constants very much more work will be required.

ABSTRACT.

In the experiments described the cathode, which consists of a horizontal copper disc perforated with two holes, is mounted in a cylindrical glass tube open at the lower end. The whole is suspended from the beam of a balance, and is immersed in a vessel of copper sulphate. The anode is a copper spiral fixed in the electrolyte some distance below the mouth of the cathode vessel. From the rate of change of weight of the suspended system during the passage of a current the ionic velocities can be determined.

DISCUSSION.

Mr. F. E. Smith admired the manner in which small difficulties had been overcome. Some years ago he had determined the electrochemical equivalent of silver with the anode suspended from the beam of a balance. If Mrs. Griffiths intended continuing these experiments, he would suggest the use of such salts as silver nitrate rather than copper sulphate.

Mr. J. H. Shaxby communicated the following remarks: It may be noted that the use of a relation, implicit in the reasoning but not actually employed, leads to a simple formula for calculating V without the necessity of separate determinations of m_1 and m_2. This saves a rather lengthy calculation, and incidentally avoids the necessity for relying on data in Landolt obtained by other workers. The relation is that the current $Ne(U+V)$ is also equal to $m_1q(U+V)$. (In fact, from the values given, $Ne=34{\cdot}36$ and $m_1q=34{\cdot}12$.) If, then, we substitute $\frac{c}{m_1q}-V$ for U in the equation

$$m_2V-m_1U-n\delta\rho V+\frac{c\rho}{qd}=W \text{ (loss in weight observed),}$$

we have
$$m_2V-m\left(\frac{c}{m_1q}-V\right)-n\delta\rho V+\frac{c\rho}{qd}=W,$$

or
$$V(m_1+m_2-n\delta\rho)=W+\frac{c}{q}-\frac{c\rho}{qd};$$

i.e.,
$$Vn(1-\delta\rho)=W+\frac{c}{q}\left(1-\frac{\rho}{d}\right).$$

The quantity δ is derived from the statement that "total mass of salt in cathode vessel diminishes at the rate of $(m_1+m_2)Av$ gms. /sec." Now this diminution is not by the elimination of salt *qua* salt, but in the form of already dissociated ions. The calculation of δ, from the variation of density of a solution with concentration, lumps together undissociated and dissociated salt. If we may suppose the ions to be of great density, the value of δ would be very small. If we neglect δ and re-calculate V, we find for experiments (12), (9), (3) and (6) respectively the values 6·339, 3·138, 4·011 and 1·561 ($\times 10^{-4}$), leading to the values for $\frac{v}{u+v}$ 0·6584, 0·6561, 0·6627 and 0·6634. For the lowest concentrations these agree with other workers' figures. Metelka's results for densities 1·019 and 1·038 suggest similarly constant values of $\frac{v}{u+v}$ for various concentrations, and are also in good agreement with Mrs. Griffiths' figures (as thus re-calculated).

Mrs. Griffiths has communicated the following comments on Mr. Shaxby's remarks: The mathematics in the second and third paragraphs appears to be correct and is interesting, but the first paragraph would seem to be somewhat misleading in that the necessity is not avoided for relying on data (dealing with concentrations) obtained by other workers. Mr. Shaxby avoids the necessity by making an hypothesis in the last paragraph which is not justifiable, for when the current has ceased the value of δ cannot depend on the process whereby the salt has been eliminated. Even during the passage of the current the process can have only an inappreciable effect on the value of δ.

XV. *Note on an Explanation of the Migration of the Ions.* *By* S. W. J. SMITH, *M.A., D.Sc., F.R.S., Assistant Professor of Physics, Imperial College.*

RECEIVED FEBRUARY 21, 1916.

1. The object of this note is to attempt to remove an imperfection from a much-used graphical "explanation" of the phenomenon known as the migration of the ions.

The explanation in question proceeds briefly as follows: It is supposed that a solution of a salt MX is being electrolysed, that M is depositing upon the cathode C while X is similarly escaping from solution at the anode A, and it is desired to show that the rate of impoverishment of the solution round C is to that round A in the ratio $v : u$ of the ionic velocities of X and M. For this purpose a diagram of the following kind is drawn to represent (i.) the initial state of the electrolyte and (ii.) its state after a time t.

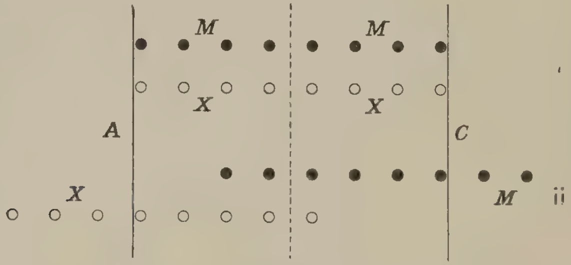


FIG. 1.

For purposes of illustration a simple ratio of u to v is chosen—*e.g.*, 2 : 3, as in the figure. It is now pointed out that the number of molecules to the left of the median line is fewer by two than the initial number, while the number to the right is fewer by three. Then it is said that it is seen in this way that three molecules are lost at the cathode, while two molecules are lost at the anode, and that, therefore, the cathode loss is to the anode loss as 3 : 2.

The same argument can be indicated more generally by a figure of the kind given below :—

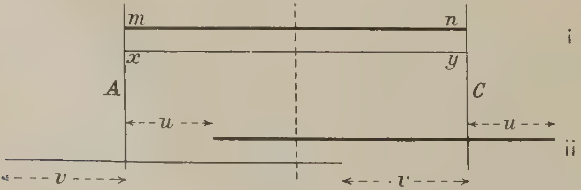


FIG. 2.

The initial string of positive ions is represented by the heavy line *mn*, and the corresponding string of anions by the lighter line *xy*. Taking *u* and *v* to be the respective velocities of the ions, the positions of the strings one second later will be as represented in the lower half of the figure, and, using the same argument as before, the decrease in the number of molecules to the left of the median line is to the decrease to the right in the ratio $u : v$.

2. The objection to this argument, however presented, is that, while it is made to give the correct result, it does not adequately represent what occurs. It ignores the cations left in solution near *C* and the anions left near *A*, and it is also silent concerning the inequality between the number of cations deposited upon *C* and of anions deposited upon *A*.* Further, even if we grant that the mechanism of electrolysis can be indicated in the simple way which the diagram suggests, molecules primarily concerned in the losses at the electrodes are omitted.

The truth of the matter is that no explanation of the relation between the electrode losses can be satisfactory if it does not emphasise the difference between the way in which the current is conveyed from one layer of the liquid to the next and that in which it is conveyed from the liquid to either electrode.

In the liquid the transference is partly by positive ions travelling in one direction, and partly by negative ions travelling in the opposite. At the electrodes, the transference is by ions of one kind only—by positive ions at the cathode and (in the simple case supposed) by negative ions at the anode.

In consequence of this, more cations are deposited at the cathode, and more anions at the anode, than those for which the ionic streams, due to the applied potential gradient, are responsible.

3. What happens may be represented symbolically in the following way :—

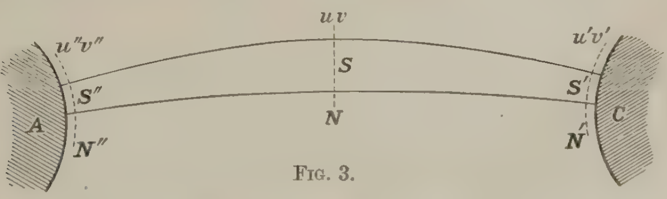


FIG. 3.

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* It is sometimes stated that the ions left unpartnered are supposed to be discharged and liberated.

In the figure let A and C represent sections of the electrodes, and let the curves extending between them represent the section of a tube bounded by current stream lines at any time t. Suppose for simplicity that the ions M and X are of equal valency and carry respectively the charges $\pm\varepsilon$. Let the potential gradient at any cross-section of the tube, of area S, be such that the ionic velocities are u and v respectively, and let N be the number of ions of each kind per unit volume near S. Let S', u', v', N' and S'', u'', v'', N'' be corresponding quantities for the sections S' and S'' in the immediate neighbourhoods of the electrodes.

Then the condition that there should be no accumulation of free electricity, in any element of volume of the tube, while the current flows, gives

$$SN(u+v)=S'N'(u'+v')=S''N''(u''+v''). \quad . \quad . \quad . \quad . \quad (1)$$

The ratio of the ionic velocities is constant since these vary in the same way with the potential gradient.*

Hence, $$u/v=u'/v'=u''/v'',$$

and, therefore, from (1)

$$SNu=S'N'u'=S''N''u'',$$

and $$SNv=S'N'v'=S''N''v''.$$

The current across any section of the tube, at the time considered, is $SN(u+v)\varepsilon$ and the quantity of electricity conveyed through the solution, in the time dt, is $SN(u+v)\varepsilon dt$. During this time the number of cations deposited upon the cathode is, by Faraday's law, $SN(u+v)dt=S'N'(u'+v')dt$. Similarly, the number of anions deposited upon the anode is $SN(u+v)dt =S''N''(u''+v'')dt$. The number of cations brought by the current to the cathode in the same time is $S'N'u'dt$, and of anions to the anode $S''N''v''dt$.

Thus we see that the number of cations deposited upon the cathode exceeds the number brought up by the current by $S'N'(u'+v')dt-S'N'u'dt=SNvdt$, and that the number of anions deposited upon the anode exceeds the number brought up by the current by $S''N''(u''+v'')dt-S''N''v''dt=SNudt$.

In seeking for the source of supply of these excess cations and anions deposited upon the electrodes we notice that, in order to satisfy the equation (1), $S'N'v'dt=SNvdt$ anions must pass outwards through S′ and that $S''N''u''dt=SNudt$ cations must pass outwards through S''.

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* For the present purpose the fact that u/v may vary with N can be ignored.

Therefore, equation (1) will be satisfied if the following processes occur :—

During the deposition of $S'N'(u'+v')dt$ cations upon the cathode, $S'N'v'dt$ molecules dissociate (ionise) in the immediate neighbourhood of this electrode. The $S'N'v'dt$ cations of these molecules are deposited along with the $S'N'u'dt$ cations carried in by the cationic stream, while their $S'N'v'dt$ anions pass away from the electrode to maintain the anionic stream.

During the deposition, contemporaneous with that above, of $S''N''(u''+v'')dt$ anions upon the anode, $S''N''u''dt$ molecules dissociate in the solution in contact with this electrode and deposit their $S''N''u''dt$ anions along with the $S''N''v''dt$ anions carried to the anode in the anionic stream, while their $S''N''u''dt$ cations pass away from the electrode to maintain the cationic stream.

In this way during the passage of $SN(u+v)\varepsilon dt$ units of electricity through the solution, $SN(u+v)dt$ cations are deposited upon the cathode, and $SN(u+v)dt$ anions are deposited at the anode. The cathode space loses $SNvdt$ molecules, and the anode space loses $SNudt$.

Hence, we see at once that the ratio of the cathode loss to the anode loss, in any given element of time, is $v : u$, and we see also at once where the " lost " molecules have gone.

4. If it be urged, against the generality of this view of what occurs, that the requisite numbers of molecules may not always be present near the electrodes, or may not always ionise spontaneously to the required extent in the interval of time considered, it should be remembered that any process other than one which keeps the quantity of free electricity in each element of volume zero will give rise to E.M.F.s tending to modify the current in such a way as to enable conduction to continue along the lines indicated.*

But, for the purposes of this note, it is both unnecessary and inadvisable to dwell upon the phenomena of polarisation, whether in the form of P.D.s within the solution or at the electrodes, which are inevitably present. Such considerations to be complete would have to take account, for example, of the fact that the ions of the solvent may also be involved. And, most of all, it has to be remembered that the diagram is only used in the many text-books in which it occurs, as a means of explaining Hittorf's method of finding the migration constant.* For this purpose the argument of §3 can be shown to be adequate by means of the following simple illustration of Hittorf's method.

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* A further reference to this point will be found, in the reply to the discussion on the Paper.

A glass tube of any convenient length and diameter is taken (quite a small tube will suffice), together with two corks through which pieces of stout copper wire are inserted centrally to act as electrodes. The tube is fixed in a vertical position with one of the corks fitted tightly into its lower end. The tube is nearly filled with a concentrated solution of copper sulphate; it adds to the instructiveness of the experiment if a saturated solution is used. The other cork, which is fitted rather loosely, is then inserted into the upper end, so that a centimetre or two of the wire which passes through it is immersed in the solution. A current from a two-volt accumulator is then passed through the solution for some hours, the lower wire being the anode and the upper the cathode. The colour of the solution round the cathode gradually disappears. The manner of the disappearance is significant.

It is easily seen that the loss of colour is not confined to the immediate neighbourhood of the wire but extends over the whole of the liquid above a horizontal plane lying near the lower end of the wire. The inferences from this are that convection currents are circulating continuously in the upper part of the tube, that one part after another of the liquid contained in this space comes into the region where the main portion of the current is flowing and that this liquid gets continuously poorer in copper sulphate because each part loses a fraction of its salt content as it moves over the electrode. There is, therefore, no difficulty in this case in seeing where the bulk of the additional molecules, required as in §3, is obtained.†

It may be interesting to add that, if a saturated solution has been used, crystals of copper sulphate can be observed round the anode at the conclusion of the experiment. These represent the "anode gain," just as the destruction of colour in the upper part of the tube represents the (equal) "cathode loss."

This experimental illustration can be made additionally instructive, from the point of view of this note, if a second tube of identical construction is arranged in series with the first. The two tubes are placed side by side and the upper electrode is the cathode in each. The solution in the second tube besides being saturated with copper sulphate contains (for example) an equivalent amount of zinc sulphate. By comparing the colours of the two cathode spaces (or the apparent colours of the electrodes as seen through the cathode liquids) from time to time after the current has begun, it becomes evident that the solution round the cathode in the second tube loses copper at the greater rate. In this tube the cationic stream consists partly of zinc ions and the amount of copper carried to the cathode per second by the current is therefore less than in the first tube. Hence, since the rate of deposition of copper on the two cathodes is the same, the solution round the cathode in the second tube has the greater demand made upon its supply of copper. The rates of loss will be, approximately, in the ratio $(v+\frac{1}{2}u) : v$, if we suppose the zinc and copper ions to be equally concentrated in the second tube, and to have approximately the same velocity.

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* Not necessarily giving $v/(u+v)$ if the ions are hydrated.

† Diffusion from below is, of course, never quite absent, and cases in which it is the only means of supply of the molecules required have, as is well known, been carefully studied.

I think experiments such as this remove any doubt about the need for distinguishing, among the ions deposited, between those ions which are carried by the potential gradient and those which are not.

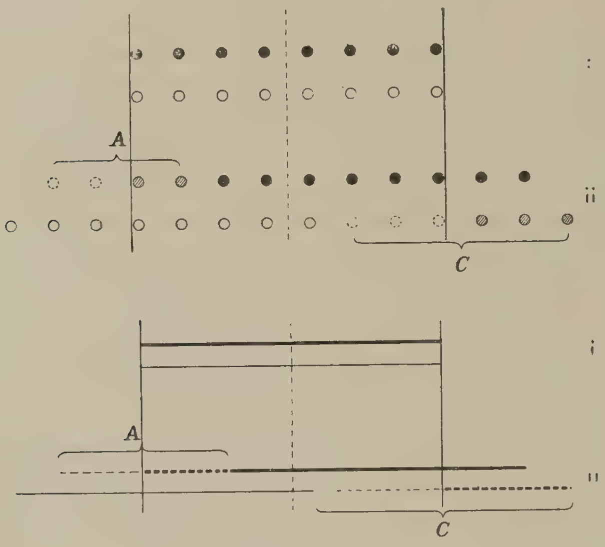
5. It has, of course, to be remembered that it is inadvisable to attempt to follow too minutely the motions of particular ions, for these, as well as the molecules out of which they come, have other motions besides those impressed by the applied electric field. The purpose of this note will, however, be attained if it shows how (subject to the limitations which any diagrammatic representation must contain) the picture usually given can be made more intelligible.

For this purpose it is only necessary to make the additions to Figs. 1 and 2 shown in Figs. 4 and 5 on p. 154.

The molecules contained within the bracket near C, in each figure, are those which actually disappear from the cathode space, while those contained within the bracket near A are those lost by the anode liquid. The ions to the right of C and to the left of A are those removed from the solution at the same time.

These diagrams show explicitly that ionised molecules of salt have to be fed into the current stream at the electrodes in order to keep it going, and it is just this essential feature of the phenomenon that the usual diagram omits.

6. It will be understood that Fig. 4 (or Fig. 5) is not intended to be more than a crude representation of any actual case.* For instance, the diagram contains no suggestion of the proportion which each electrode space (of variable concentration) bears to the total volume occupied by the electrolyte. The figure could be improved in this respect by replacing the median line by two parallel lines with a gap between them to represent the interior of the electrolyte. And, as a further improvement, the ions might be shown (or considered to be) less widely spaced in this link between the two electrode regions. For, in general, the concentrations N' and N'' (Fig. 3) must be less than N. If the current is to flow at a given rate for a finite interval, the rate of supply of fresh molecules to each electrode region must equal the rate of removal which the current involves. Diffusion is the only steady source of supply of these fresh molecules. Therefore the concentrations near the electrodes must always become definitely less than that in the interior of the electrolyte. The necessary differences of concentration could, however, be small if the current were not large



Figs. 4 & 5.

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* Apart from the fact that in practice there is usually an anode gain instead of an anode loss.

and if, by gravitational convection or otherwise, the original concentration of the solution were maintained, as far as possible, along the whole path of the current. The concentration gradients near the electrodes (which determine the rates of supply of fresh molecules) could then be appreciable even when the actual differences of concentration, between the main solution and the electrode layers, were small.*

ABSTRACT.

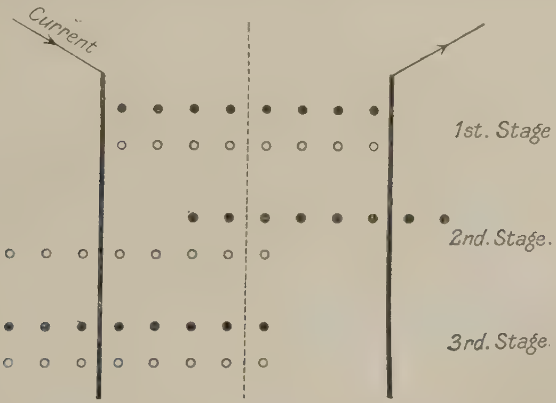
The object of this Note is to show how a familiar diagram, appearing in many text-books, can be improved in a way which makes it easier to appreciate what happens at the electrodes in the simpler examples of Hittorf's method of determining the migration constant. An attempt is made to give precision to an idea which is sometimes vaguely expressed and frequently ignored.

DISCUSSION.

Mr. D. Owen considered that the usual graphical method expressed the integral effect simply and satisfactorily unless pressed in detail. The analysis of paragraph three of the Paper, whilst adding precision to the conclusions, did not modify them or "explain" them. The fact of the existence of a volume distribution of electricity near to the electrodes implied an increased potential gradient which played a part in the actions occurring in those regions.

Dr. Willows suggested that, if Mr. Owen's view were correct, it should be possible to detect the potential gradients to which he referred.

Mr. F. E. Smith remarked that Dr. Smith's Paper dealt with a real difficulty, and one which teachers of electricity had to face. He remembered giving lectures on the subject to very elementary students, and, feeling dissatisfied with the explanatory diagrams in text-books, had adopted another form of explanation. In dealing with the phenomenon the negative ions were never said to be discharged. The general argument followed was to regard matter as being in four states—solid, liquid,



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* *See also* p. 156.

gaseous and ionic. It was already conceded from analogies that copper ions and metallic copper differed because of a difference of electrical energies. Conversion from one into another could be brought about by adding or subtracting electrical energy. Thus, in the electrolysis of copper sulphate solution with copper electrodes, the electrode at high potential lost energy by conversion of a part of itself into positive ions, and the negative electrode gained energy from the solution due to positive ions giving up their charge and being converted into the metallic form. Taking Dr. Smith's Fig. 1 of the Paper, the process of electrolysis would be explained by adding to it the third stage shown in the figure. The negative ions were never discharged. The copper ions put into solution from the positive electrode were associated with them, and are shown in the figure. The diagram shows (1) the changes of concentration at the two electrodes, (2) that the mean concentration of the electrolyte is unaltered, (3) it can be used to obtain the migration ratio.

Dr. SMITH, in reply, said : In the original draft of the Note, as submitted to the Society, he had hazarded the opinion that perhaps the Authors, who used the diagram, wished it to be understood that the excess ions shown at the ends of the chains were removed by excess potential gradients. He had deleted this conjecture, and had substituted a footnote (which was, in fact, a quotation), because he had been unable to find any proof that this was the view taken. In any case it was unsatisfactory. Mr. Owen seemed to imagine that there was some virtue of simplicity about this view which made the analysis of §3 unnecessary. This was not the case. The problem was not simyly to state how a Hittorf migration experiment might be supposed to begin. It was as necessary to show clearly what occurred while it continued. This was the object of the Note. The analysis of §3 was merely a general method of expressing the fact that some of the ions which take part in the electrolytic process are fed into the circuit near the electrodes, and are not brought there by the potential gradients. Views which "explain" the facts, while ignoring this, have been the cause of needless confusion in the minds of students. The analysis of §3 showed, for example, that conduction could not proceed as it began unless for every $(u+v)$ cations deposited v cations and v anions were fed into the circuit at the cathode. If the cathode region had to draw upon itself for this supply of ions, the concentration there would rapidly fall and the "polarisation" at the cathode would rise in accordance with the well-known relation connecting the contact potential difference with the concentration. Diffusion, however, always played an essential part. When it was promoted by convection, a slight reduction in the concentration of the solution round the cathode would be enough to set up an appreciable diffusion current which would be maintained in the way described in §4 of the Note. This was the current which supplied the necessary molecules to the cathode space. The relation between this diffusion current and the electric current could be represented by the equation $kn=vi/(u+v)e$, where k is a diffusion constant, n is the concentration gradient at the cathode, i is the electric current density, and e is the ionic charge.

With regard to the question raised by Dr. Willows, he was of the opinion that measurable potential differences of the kind described did not exist. He was glad that the Chairman was of the same opinion as himself with respect to the diagrams and descriptions usually given.

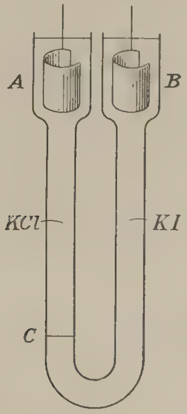
XVI. *A Method of Exhibiting the Velocity of Iodine Ions in Solution.*

By S. W. J. Smith, *M.A., D.Sc., F.R.S., Assistant Professor of Physics, Imperial College.*

Received March 9th.

I have shown the following experiment in lectures on electrolysis at the Imperial College for many years, since 1900 in fact; but have not described it hitherto.

It is of the same general kind as those first made by Sir Oliver Lodge, and subsequently by Whetham, Masson, Steele, Denison and others; but it will be seen, by those familiar with their work, that it has certain distinctive features of its own to which, perhaps, it is worth while to draw attention. I am led to offer the following account of the experiment by the reminder from the President, at the last meeting, that interesting experiments are always welcomed by the Society.



For the sake of brevity, I will confine myself to a description of the method of obtaining approximate results and omit the precautions which must be taken if great accuracy is desired.

The apparatus, in its simplest form, is represented in the diagram. The containing vessel is a U-tube with widened ends as shown. The diameter of the tube may be about 0·5 cm. or less. The cross-section of the tube should be fairly uniform and, in particular, should not be less at the bend than in the limbs. Either 25 cm. or 50 cm. is a convenient (total) length for the tube if it is desired to use it in connection with an ordinary lighting circuit voltage of 100, or thereabouts, and to obtain a rapid estimate of the velocity of the ions.

The electrodes (at A and B) are, preferably, of platinum foil. The liquids used are equally concentrated solutions, containing —*e.g.*, either 0·2 gm. or 0·1 gm. mol. per litre, of potassium chloride and potassium iodide respectively. The tube may be filled, in the way described by Whetham, by closing the end of the A limb while the B limb is filled and then closing B while the A limb is filled.

The novelty of the experiment lies in the method of exhibiting the line of separation between the solutions.

For this purpose a small quantity of mercuric chloride (corrosive sublimate) is dissolved along with the KCl. [In the endeavour to maintain symmetry an equal quantity of the same salt may be added to the KI.]

If, under these circumstances, the filling is carefully performed, a thin yellow disc of mercuric iodide, precipitated by the action of the KI upon the $HgCl_2$ contained by the KCl, will appear at the junction between the electrolytes. Even if the filling is performed rather carelessly, this disc soon becomes sharply defined because the mercuric iodide, although insoluble in KCl, dissolves in the KI and therefore cannot exist continuously except at the boundary between the two electrolytes.

When the line of separation has become well defined, the electrodes at A and B are connected to the source of supply, that at A being made the anode. The boundary at C immediately begins to move upwards. It travels as an extremely thin horizontal disc, which can be located very accurately and projected with ease. Moreover, under the conditions already mentioned, the disc will move at speeds of the order of 1 mm. per minute, so that its motion can be followed without difficulty by a large audience, and an approximate estimate of its velocity can be obtained in a few minutes.

To illustrate what happens, observations of the position of the disc, taken at intervals of 5 minutes for an hour after the E.M.F. was applied, are tabulated below. The potential gradient was about 3·7 volts per centimetre. The current was reversed, B being made the anode, after it had run for 30 minutes. The gradual rise in the velocity (shown in the difference column) is due to the rise in temperature of the electrolytes (and resulting increase in the mobility of the ions) as the experiment proceeds. For obvious reasons the rise in temperature is most rapid at the beginning of the experiment.

Mins.	Cm.	Diff.	Mins.	Cm.	Diff.
30	13·6		30	13·6	
		0·68			0·54
25	12·92		35	13·06	
		0·72			0·71
20	12·2		40	12·35	
		0·67			0·74
15	11·53		45	11·61	
		0·55			0·73
10	10·98		50	10·88	
		0·51			0·70
5	10·47		55	10·18	
		0·47			0·72
0	10·0		60	9·46	

The positions of the line of separation were determined by means of a millimetre scale placed alongside the tube.

The possibility of observing the reverse motion of the anions is due to the fact that the chlorine gas separated at A soon travels down the tube in sufficient quantity to decompose a fraction of the KI with separation of iodine. In consequence the solution below the disc soon becomes distinctly yellow. The coloration so produced permits observation of the retreat of the line of separation between the iodide and the chloride when B is made the anode.

Otherwise the rate of descent could not be measured over any considerable range, for, generally, the yellow disc of mercuric iodide disappears before very long when the current is reversed. This is no doubt due to the fact that when the iodine ions are moving downwards they are moving away from the mercuric chloride which can only reach them by diffusion (or by convection due to irregular heating). The summit of the yellow coloration, although not so easily determinable as that of the yellow disc, can, however, be fixed with fair accuracy, and so its velocity can be determined. It descends at the same rate as the iodine ions because, the solubility of iodine in KCl being negligibly small compared with its solubility in KI, the dissolved iodine retreats with the iodide.

The course of events being as indicated above, I may add the results of an attempt, made with the same apparatus on another occasion, to obtain an estimate of the velocity of the ions, at some definite temperature, in centimetres per second under a gradient of 1 volt per centimetre. The solutions (as in the previous case) contained 0·2 gm. mol. per litre. The current was allowed to run for about 20 minutes, in order to avoid the rapid rise in temperature at the beginning, before observations were begun. Similarly, the reversed current was allowed to run for some time before the second set of observations was made. The distance traversed by the line of separation during the first half hour of the experiment (measured by means of a small cathetometer) was 4·13 cm. The distance traversed in the second half hour was 4·53 cm. The difference was probably due mainly to a higher mean temperature in the second half of the experiment. On this occasion an ammeter was included in the circuit. The reading rose slowly during the observations. Its mean value during the hour was 0·03 ampere. The specific resistances of the electrolytes were measured at 10°C. (the temperature of the room) just before the tube was filled. The mean value was approximately 55 cm. ohms. The value of the current immediately after the circuit was completed was 0·023 ampere. The area of cross-section of the tube was about 0·31 sq. cm. Hence the initial potential gradient in the tube was approximately

$$(0{\cdot}023\times 55)/0{\cdot}31=4{\cdot}1 \text{ volts per centimetre.}$$

Assuming the potential gradient to have remained constant throughout the experiment, the fact that the mean current was about 30 per cent. higher during the observations than at the first completion of the circuit means that the specific resistance of the electrolytes was about 30 per cent. less than its initial value at 10°C.—*i.e.*, that the average temperature of the electrolytes during the observations was about 25°C. Hence the velocity of the anions, iodine and chlorine, as determined in this way, is about

$$(4{\cdot}13+4{\cdot}53)/(3{,}600\times 4{\cdot}1)=0{\cdot}00059 \text{ at } 25^\circ\text{C.}$$

in cm. sec.$^{-1}$ per volt cm.$^{-1}$. But, of course, if accurate and not rapid determinations were required, much smaller potential gradients could be employed. The heating effects would, similarly, be less troublesome if more dilute solutions were used.

It may be noticed in connection with the method that solutions of KCl and KI of equal molecular concentration become electrochemically more nearly identical the more dilute they are. Even at moderate concentrations the conductivities are the same within a few per cent. Solutions of equivalent strength are, therefore, practically equally ionised, and the velocity of the iodine ions in the one is practically equal to that of the chlorine ions in the other. A consequence of this is that not only is the potential gradient the same in both solutions (if the tube is of uniform cross-section) but there is also no contact potential difference between them. These were the facts which led me to endeavour to find a simple method of fixing the line of separation between solutions of the salts in question.

Another device which can be used, and was the first that occurred to me, consists in adding a small quantity of silver nitrate to the KCl solution and re-dissolving the slight precipitate of silver chloride, which is formed, by the addition of a little ammonia. The upward movement of the iodine ions is now exhibited by the formation of silver iodide which is practically insoluble in ammonia. The progress of the ions is not as interesting to watch as in the case described above, because, the silver iodide not being soluble in the excess of KI, the point which the iodine ions have reached at any moment is not now represented by a thin disc but by the summit of the general cloudiness produced by the precipitated iodide of silver.

ABSTRACT.

Dilute solutions of potassium iodide and potassium chloride of equi-molecular concentration have almost the same electric conductivity. They are, therefore, of interest in connection with the direct measurement of ionic velocities. The Paper describes a simple method of observing their common boundary. For this purpose a little mercuric chloride is added to the potassium chloride solution. An extremely thin layer of mercuric iodide then forms where the two solutions meet. The method is particularly convenient for lecture purposes, and an approximate value of the ionic velocity can be obtained in a few minutes.

The Paper gives examples of the use of the method. The current is first passed in the direction which causes the iodine ions to travel towards the chloride. The chlorine liberated at the anode in this case supplies a means of re-determining the velocity of the ions when, the current being reversed, they move in the opposite direction.

XVII. *The Electrical Capacity of Gold-leaf Electroscopes.* *By* T. Barratt, *D.Sc., A.R.C.S.*

Received March 20, 1916.

I. Introduction and Historical.

The modern gold-leaf electroscope has for some considerable time been employed by workers in radioactivity as an instrument of precision comparable with that of other instruments used in electrical measurements. Many workers in other branches of physics, however, still appear to regard the instrument as of merely historical interest. It is the experience of the author that with the help of the gold-leaf electroscope measurement of potential can be made with an accuracy of, at any rate, 1 per cent. between, say, 50 and 300 volts, the limits depending on the particular instrument. The gold-leaf electroscope possesses many advantages over the usual type of electrometer. The latter is exceedingly troublesome to set up and to work, and requires very great care in maintaining satisfactory insulation. Its capacity is many times that of the electroscope, which can, therefore, measure much smaller currents. [*See* Paper by G. W. C. Kaye, Phys. Soc. "Proc.," 23, p. 209, 1911.] In addition, the electroscope is much cheaper, takes up very little space, is easily transported and can be used in any position.

Methods for the determination of the capacity of the gold-leaf electroscope have been given by F. Harms* and by Lichtenecker.† In the measurement of such small capacities the usual commutator methods cannot be employed. Accurate and well-insulated standard condensers of the same order of capacity as that of the electroscope cannot be obtained; and, again, the capacity of any connecting wires, switches, &c., are of the same order of magnitude as that of the leaf system itself, and are not known with any degree of accuracy. In order to overcome the latter difficulty, Harms‡ allowed drops of mercury, alcohol or water to fall from a charged capillary tube into an ionisation vessel connected with the electroscope. Obviously the method cannot be employed with an electroscope not possessing such an ionisation vessel. An experiment often took 18 minutes to perform, and corrections had to be made for loss of potential during that time. It would also appear that a further correction was necessary for electrical energy produced by the fall of the drops of liquid from a great height (over 100 cm.). Lichtenecker* attached a sphere to the electroscope by a long wire, and by measuring the capacity of the electroscope, sphere and wire for various lengths of the wire deduced the capacity of the electroscope alone. In both of these methods elaborate apparatus was necessary, and the individual results differed in some cases by as much as 10 per cent.

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* "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik.," 10, p. 816, March, 1903.

† "Phys. Zeit.," p. 516, 1912.

‡ "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik.," 10, p. 816, March, 1903.

The method that appears to be generally used in the laboratory is to charge the electroscope to a known potential, allow it to share its charge with a small sphere of a few cms. diameter, and deduce the capacity of the electroscope from the observed drop of potential. Unfortunately, however, the capacity of the electroscope when in contact with the sphere is very different from its true capacity, and Harms† remarks that results differing by 25 per cent. will be obtained by this method. For example, the joint capacity of two spheres in contact, each of radius a, is not $2a$, but $2a \times \log 2$.‡ If the spheres are of radii a and b, and if b/a is large, the capacity of the smaller sphere is not a, but $\frac{a^2}{b} \cdot \frac{\pi^2}{6}$.

It is impossible, however, to obtain a similar formula for the combined capacity of a sphere and a conductor of such a shape as the rod and leaf of a gold-leaf electroscope.

II. Apparatus and Method of Experiment.

Preliminary experiments showed that the use of a parallel-plate air condenser in place of a sphere overcame this difficulty. There is nothing new in the method except in some of its details. For example, contact is made between condenser and electroscope, not once, but if necessary several times, the electroscope being earthed each time after contact. A long thin copper wire (gauge 30) is attached to the insulated plate of the condenser, which consists of plate glass covered with thin tinfoil (the two sheets of tinfoil facing each other), and insulated by three pieces of sulphur, whose thickness is accurately measured by a micrometer screw gauge. If the sulphur be scraped by a sharp penknife its insulating powers are almost perfect. The condenser is surrounded by a guard ring, so that its capacity is known with accuracy. In the present series of experiments a second condenser (without a guard ring) was used, its capacity having been first carefully compared with that of the guard-ring condenser. The capacity included that of the attached copper wire. It was found that the reading of the leaf of the electroscope was very nearly the same when joined to the condenser by the connecting wire as when the latter was disconnected and earthed. The fact that nearly all the lines of force of the condenser are crowded between the plates no doubt accounts for this.

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* "Phys. Zeit.," p. 516, 1912.

† "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik.," 10, p. 816, March, 1903.

‡ J. J. Thomson, "Elemts. of Elec. and Mag.," 3rd edition, p. 181.

The necessary small correction for the difference between the capacity of the electroscope as obtained by the above method and its true capacity (*i.e.*, its capacity when the usual conductors in the vicinity of the leaf system are all earthed) is easily obtained. It is found by experiment that the potential, as indicated by the position of the leaf, is slightly reduced when the attached wire from the condenser is disconnected and earthed. The percentage reduction is found to be the same, within errors of experiment, for all values of the potential. It varies slightly for different electroscopes, but is never more than about 2 per cent. If the potential is reduced from V to V' on removing and earthing the wire, then, as the charge on the leaf system is unaltered, the capacity is changed from C to C', where $C'V'=CV$, or true capacity $C'=CV/V'$.

For example, in the case of the electroscope examined in Section III. (i.), $V=300$, $V'=294$, $C=7{\cdot}13$.

Hence, true capacity$=390\times 7{\cdot}13/294=7{\cdot}27$ cm.

The electroscope and reading microscope were firmly secured to a rigid bench. A vernier attached to the microscope, and reading to one-twentieth of a millimeter, moved along a horizontal scale, and the reading of the leaf was obtained at potentials of 20, 40, 60, . . . 300 volts, as given by a battery of small accumulators, standardised by a voltmeter. A curve was then drawn connecting potential of leaf and reading of microscope scale. Such a curve is given in Fig. 1.

The battery, which has proved exceedingly satisfactory, was made in the laboratory at a very small cost. The cells were arranged in rows of 10, and could all be charged together by about 12 or 13 accumulators of the usual laboratory type.

The electroscope and condenser were connected and charged by means of an ebonite rod to a known potential, given by the reading on the scale and by reference to the curve. The wire from the condenser was disconnected from the electroscope with the help of a rod of sulphur, and the electroscope earthed by means of a copper wire soldered to the gas pipes. The condenser was again connected to the electroscope, disconnected, and the electroscope earthed. This process of alternate earthing of the electroscope and sharing the charge of the condenser was repeated as many times as necessary, and the capacity of the electroscope deduced. It is to be observed that the connecting wire does not form a part of the capacity to be measured, but is included in that of the condenser. The experiment takes only a few seconds, so that no correction is necessary for loss of charge.

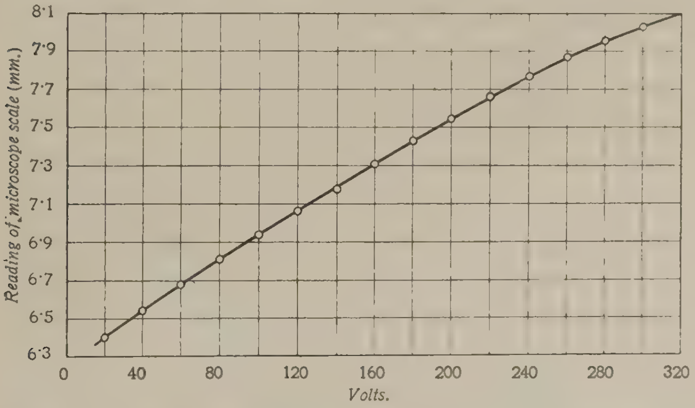

Fig. 1.—Curve Connecting Potential of Leaf and Reading on Microscope Scale.

If V is the original potential of the condenser and C its capacity, v_n the final potential of the system after n alternate earthings and re-chargings as above, and c the required capacity of the electroscope, it can easily be deduced that

$$v_n = \left(\frac{C}{C+c}\right)^n . V,$$

or

$$\log (C+c) = \log C + \frac{1}{n}(\log V - \log v_n).$$

III. Determinations of Capacity.

1. *Cubical Lead Electroscope.*—The edge of the electroscope was of length 20 cm. A central copper rod, length 18 cm.,

passing through sulphur in a glass cylinder 5 cm. long, 1·5 cm. diameter, carried a leaf 4·5 cm. long, 1 mm. wide.

TABLE I.

Dimensions of plates of air condenser: 35 cm. × 24 cm.; distance apart, 0·480 cm. Capacity of condenser and wire = 144 cm. Correction for obtaining "true capacity" = 2 per cent. [*See* Section II.]

First potential, V.	Second potential, v_n.	No. of charges n.	Capacity c of electroscope.	True capacity c' of electroscope.
100 volts	79 volts	5	6·95 cm.	7·09 cm.
100 ,,	62·5 ,,	10	6·93 ,,	7·07 ,,
100 ,,	49·5 ,,	15	6·91 ,,	7·05 ,,
150 ,,	118·0 ,,	5	7·10 ,,	7·24 ,,
150 ,,	92·5 ,,	10	7·13 ,,	7·27 ,,
150 ,,	73·0 ,,	15	7·08 ,,	7·22 ,,
200 ,,	122·0 ,,	10	7·29 ,,	7·43 ,,
250 ,,	153·0 ,,	10	7·24 ,	7·38 ,,
300 ,,	185·0 ,,	10	7·13 ,,	7·27 ,,

2. *Emanation Electroscope.*—By Cook, of Manchester, after a pattern by Sir E. Rutherford. The emanation chamber was cylindrical, of height 14 cm., and was surrounded by a cylindrical chamber of the same diameter and 9·2 cm. in height. The rod carrying the leaf and penetrating also the lower chamber was provided with a disc of 5 cm. diameter, opposite which was a similar movable disc, so that the capacity could be varied. The leaf itself was 5 cm. long and 3 mm. wide. The results given in Table II. were obtained with the discs at their maximum distance apart.

TABLE II.

Capacity of condenser and wire = 144 cm. Correction for obtaining true capacity = 1·5 per cent.

First potential, V.	Second potential, v_n.	No. of charges n.	Capacity c of electroscope.	True capacity c' of electroscope.
240 volts	202·5 volts	3	8·39 cm.	8·51 cm.
280 ,,	249·5 ,,	2	8·55 ,,	8·68 ,,
280 ,,	235·5 ,,	3	8·55 ,,	8·68 ,,
280 ,,	222·5 ,,	4	8·52 ,,	8·65 ,,
280 ,,	210·0 ,,	5	8·53 ,,	8·66 ,,

With the movable disc as near as possible to the fixed disc, the capacity was increased in the ratio of 1·24 : 1.

[In this electroscope (kindly lent by Mr. F. H. Glew) the rod carrying the leaf had a backward slope, so that at about 150 volts the leaf remained very nearly in contact with the rod.]

3. *Small Cubical Lead Electroscope.*—This electroscope, of 10 cm. edge, was insulated by a sulphur bead *inside* the instrument, and charged by means of a metal charger, C (Fig. 3). This charger was well insulated by sulphur at S, and was of total length 13 cm. The rod carrying the leaf was 6 cm. long and the leaf itself was 4 cm. in length and 1 mm. wide. The joint capacity of leaf system ($=c$) and charger ($=c'$) was first determined in the usual way. Then the capacity (c') of the charger alone was measured as follows: The condenser, leaf system and charger were raised to potential V as given by the deflection of the leaf. The condenser was disconnected and leaf and charger earthed. The charger was disconnected from the leaf system, charged from condenser and earthed n times. Finally, all three were connected again, and their final potential, v_n, observed. Under these circumstances it can be calculated that

$${}_nv=\frac{C^n}{(C+\overline{c+c'})(C+c')^{n-1}}\cdot V,$$

or $$\log(C+c')=\frac{1}{n-1}\{n\log C+\log V-\log(C+\overline{c+c'})-\log v_n\},$$

from which c', the capacity of the charger alone can be obtained. The results of the determinations are given in Table III.

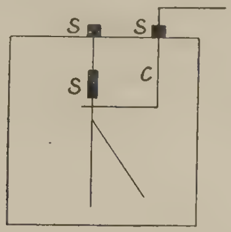

FIG. 2.—ELECTROSCOPE WITH CHARGER C.
S S S = Sulphur Insulation.

TABLE III.

Correction for obtaining "true capacity" = 2·2 per cent.

(*a*) *Capacity of Leaf System and "Charger."*

First potential, V.	Second potential v.	No. of charges.	Capacity of leaf charger (c).	True capacity (c').
300 volts	242·5 volts	10	3·80 cm.	3·17 cm.

(*b*) *Capacity of "Charger" alone.*

First potential.	Second potential.	No. of charges.	Capacity of "charger."	True capacity of "charger."
300 volts	256 volts	10	2·22 cm.	2·27 cm

(*c*) Hence, *true capacity of leaf system alone* = 3·17 — 2·27 = 0·90 cm.

4. *Ionisation Vessel and Gold-leaf Electroscope.*—The electroscope examined in Section III. (1) was connected with an "ionisation vessel," V (Fig. 3). This vessel was of cubical form, of edge about 16 cm. A radioactive substance (uranium oxide) could be placed on a square plate, A, of area 64 sq. cm., and a similar plate, B, parallel with A, was connected to the leaf system of the electroscope E.

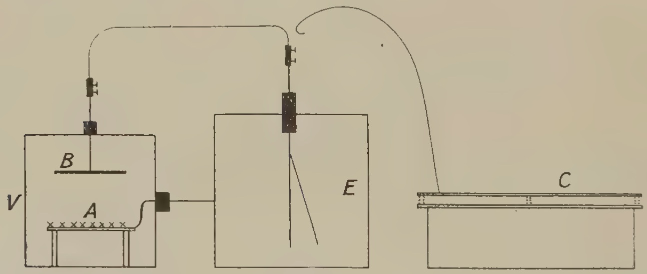

FIG. 3.

V=Ionisation vessel. E=Electroscope. C=Condenser.

A common method of measuring the capacity of a system including an "ionisation vessel" and electrometer is to observe the rate of fall of potential (as given by the electrometer) due to the ionisation produced between two parallel plates, A and B, (*a*) when connected with a condenser of known capacity, (*b*) when the condenser is disconnected.

In order to compare this method with the one described in the present Paper the capacity of the system was determined by both methods.

If C is the capacity of the condenser, and c that of the ionisation vessel and electrometer, T and t the times taken for a given fall of potential with the condenser (*a*) connected, (*b*) disconnected ; then

$$\frac{C+c}{c}=\frac{T}{t}, \text{ or } c=\frac{Ct}{T-t}.$$

Capacity of Ionisation Vessel and Electroscope.—(1) By measuring rate of fall of potential due to uranium oxide. Potential fell from 300 volts to 211 volts, (*a*) with condenser of capacity 144 cm., in 505 seconds ; (*b*) without condenser, in 58 seconds.

First potential, V.	Second potential, v.	Time with condenser, T.	Time without condenser, t.
300 volts	211 volts	505 secs.	58·0 secs.
300 ,,	187 ,,	634 ,,	71·5 ,,

The values for the capacity from these observations are 18·68 cm. and 18·31 cm. respectively ; or, when correction (0·9 per cent.) is made for earthing wire from condenser, 18·85 cm. and 18·47 cm. respectively.

(2) By the method of this Paper.

First potential, V.	Second potential, v.	No. of charges.	Capacity, c.	True capacity, c'.
300 volts	208 volts	3	18·70 cm.	18·87 cm.
300 ,,	185 ,,	4	18·50 ,,	18·67 ,,

Satisfactory agreement is thus obtained in the results given by the two methods.

IV. Discussion of Results.

The consistency of the results enumerated in Section III. may appear somewhat surprising to one not acquainted with the possibilities of a modern gold-leaf electroscope. If proper precautions be taken, a particular experiment can be repeated again and again with practically the same result, and the conditions can be widely varied without much alteration in the final value obtained for the capacity of the electroscope. The divergence of the leaf appears to have very little effect on the capacity of the system as a whole, except, perhaps, when the leaf is nearly in contact with the rod supporting it, in which case the capacity would appear to be slightly lower. This may, however, be due to a decrease in sensitiveness with the leaf in such a position, though Harms[*] obtained in some cases a similar result. It is worthy of notice that the comparatively large capacity of the standard condenser employed—which would be a serious drawback in other methods—presents no difficulty in the method of the present Paper, provided that contact be made between condenser and leaf system a sufficient number of times. With such small capacities as those dealt with here very small ionisation currents can be accurately measured. For example, in the case of the electroscope of capacity 0·90 cm., the ionisation within the vessel reduced the potential from 300 to 280 volts (corresponding to 20 divisions of the microscope scale) in about an hour. This corresponds to a current of approximately $1{\cdot}6 \times 10^{-13}$ ampere.

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[*] Loc. cit.

V. SUMMARY.

The capacities of gold-leaf electroscopes of various patterns have been determined by a method which depends upon obtaining the relation between the divergence of the leaf and the potential applied to it, and the observation of the fall of potential of the leaf system when it shares its charge a convenient number of times with a standard parallel plate air condenser. It is found that the capacity is practically independent of the amount of divergence of the leaf, except when this divergence is very small, in which case the capacity becomes slightly lower. Ionisation currents of the order 10^{-13} ampere can be accurately measured by an electroscope of capacity about 1 cm. For some purposes the gold-leaf electroscope possesses marked advantages over the quadrant electrometer. The method employed was found to give satisfactory agreement with the results obtained by another method.

ABSTRACT.

A gold-leaf electroscope is frequently used to compare exceedingly small ionisation currents. For this purpose it is much more sensitive than a quadrant electrometer. If the capacity of the electroscope is known then the absolute value in amperes of the ionisation current can be deduced. A method is described for measuring the capacity of a gold-leaf electroscope, the method depending on sharing the charge of a parallel plate air condenser of measurable capacity as many times as necessary, and deducing the capacity of the electroscope from the observed drop of potential. The method gives consistent results when the experimental conditions are widely varied. The amount of deflection of the leaf appears to have little influence on the result.

DISCUSSION.

Mr. A. CAMPBELL: The consistency of Dr. Barratt's results shows that the modern gold-leaf electroscope is an instrument of precision and justifies the use of the simple method of divided charge for measuring its capacity. The method, however, tends to make the capacity seem more constant at different readings than it really is. When a plate condenser without a guard-ring is used, the edge correction can be obtained by Kirchhoff's formula.* But standard variable air condensers marked in micro-microfarads from about 30 up to 200 are now to be had in this country, and form very convenient standards of small capacity. The capacities of ordinary electrostatic voltmeters are not very high, that of a 100-volt Kelvin or Ayrton-Mather instrument being of the order of 70 micro-microfarads. Their large variation with the reading shows that, unlike the gold-leaf type, these instruments have very little ineffective capacity. For the measurement of small capacities the Carey Foster method seems the most convenient, and it gives the power factor at the same time. With 20 volts on the condenser at a frequency of 800 ~ per second, a capacity of 5 micro-microfarads can be measured with an accuracy of about 1 per cent. It is a pity that the author gives his results in mixed units, the voltages being in electromagnetic units (volts) and the capacities in electrostatic units ; this can only lead to confusion. The practical system of volts, amperes, coulombs, farads, &c., is sufficient for all actual measurements.

Capt. C. E. S. **Phillips** observed that the experiments in which the capacity of a system containing an ionisation vessel was compared by two methods showed that the capacity of a condenser with ionised air between the plates was not different from its capacity with unionised air as dielectric.

Prof. G. W. O. **Howe** suggested that the reason the capacity of the electroscope was uninfluenced by the vicinity of the charged wire from the condenser was that the capacity of the wire was small ; it had nothing to do with the lines of force of the condenser.

Dr. **Barratt** : The edge effect in the condenser used was very small, as the plates were each of area 840 sq. cm. and only 0·48 cm. apart. This was, however, allowed for by comparison with a guard-ring air condenser. The capacity of most gold-leaf electroscopes is of the order of 1 micro-microfarad—*i.e.*, only 1/50 to 1/100 of that mentioned by Mr. Campbell. The air condensers which Mr. Campbell describes are of capacity 50 to 200 times that to be measured, which would be a great objection in other methods than that in the Paper. Carey Foster's method appears to become less accurate as the capacity to be measured approaches those dealt with in the present research. The apparatus, again, is more costly and less simple. The mixing of the units was due to the fact that the measurements were simply put down in the particular system of units employed in each measurement. Prof. Howe's alternative explanation of the want of effect of the charged wire appeared to be only another way of expressing the same fact. In the case of a charged sphere in contact with the electroscope the capacity of the latter is influenced by the lines of force radiating from the sphere, while in the case of the condenser the connecting wire is of comparatively small capacity, and is connected, therefore, with fewer lines of force.

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* Berlin "Akad. Monatsberichte," p. 144, 1877.

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CONTENTS.

PAGE

XII. Experiments on the Flow of Heat in Metal Sheets. By Sidney Skinner, M.A., Principal of the South Western Polytechnic Institute, Chelsea 119

XIII. The Absorption of Gas by Quartz Vacuum Tubes. By R. S. Willows, M.A., D.Sc., and H. Trevelyan George, M.A. 124

XIV. A New Method of Determining Ionic Velocities. By Constance Harrison Griffiths, B.Sc., Research Student, Birkbeck College 132

XV. Note on an Explanation of the Migration of the Ions. By S. W. J. Smith, M.A., D.Sc., F.R.S., Assistant Professor of Physics, Imperial College 148

XVI. A Method of Exhibiting the Velocity of Iodine Ions in Solution. By S. W. J. Smith, M.A., D.Sc., F.R.S., Assistant Professor of Physics, Imperial College 157

XVII. The Electrical Capacity of Gold-leaf Electroscopes. By T. Barratt, D.Sc., A.R.C.S. 162